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INELASTIC ION-SURFACE COLLISIONS.
Ion Neutralization on Intermetallic Surfaces

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Ion scattering and direct recoil spectrometries were used to investigate electronic excitation and charge transfer processes occurring during rare gas ion bombardment of CuLi alloy. Excitations in the close encounter appear to be governed by the degree of inner shell mixing between the colliding pair. Excitations in the outgoing trajectory are governed by the probabilities of Auger and resonant charge exchange between the scattered or recoiled particle and the surface. Measurements of the vacuum ultraviolet photon emission of the scattered and recoiled particles proved to be unsuccessful due to low photon yields. The ion induced surface damage to transition metal fluoroanions was investigated by XPS and UPS. Ion bombardment reduces the transition metal atom to lower oxidation states, in some cases all the way to the metal. These results are consistent with the thermal spike model of ion damage. The dissociation of molecular N_2^+ ions upon reflection from gold and graphite surfaces was investigated by energy analysis of the

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scattered molecular and atomic ion flux. The collision induced dissociation appears to proceed by electronic excitation of the N_2^+ to dissociative electronic states in the close encounter.

Table of Contents

iii

Objectives:

The objectives of this contract are to characterize the fundamental physical and chemical processes occurring in ion-surface reactions and to apply these to the fundamental problems pertinent to spacecraft orbiting the earth. The determination of these elementary processes will enable the elucidation of the reaction mechanisms involved in such hostile environment phenomenon as vehicle glow and surface corrosion. The observation of vehicle glow from the space shuttle is one example of such a reaction in a hostile environment (1-5). The origin of the emission is not understood, however, it may arise from reactions of reactive species with the spacecraft surfaces or with implanted or absorbed species on these surfaces. It has been proposed (6) that N and O can react on the spacecraft surface to produce excited NO which decays by photon emission yielding a glow phenomenon. The laboratory investigation of ion-surface reactions will provide insight into the fundamental physical and chemical processes giving rise to the glow phenomenon as well as such processes as surface degradation and erosion encountered by spacecraft. In order to obtain a complete understanding of ion surface processes, it is necessary to characterize the chemical and physical state of the scattered and sputtered particles as well as the chemical state of the resulting damaged surface. With these goals in mind, research initially was planned in the following areas.

1

(i)   The characterization of the scattered and sputtered particles and their internal energies resulting from medium energy (1-10 keV) ion bombardment by direct recoil spectrometry and VUV emission spectroscopy.

(ii)   The characterization of surface damage to multi-component targets from medium energy ion bombardment.

(iii)   The determination of the kinematics of polyatomic ion scattering from surfaces.

The progress in each of these areas is discussed below.

I.   **Vacuum Ultraviolet Emission Spectroscopy of Sputtered Ions and Particles**

Initial studies of vacuum ultraviolet (VUV) photon emission of sputtered particles have used very high primary beam energies and ion fluxes (300 keV, 200 μA)(7-10).   Little work has been done in the medium energy (1-10 keV) range.   Preliminary studies in this laboratory (11) have shown the possibility of measuring the VUV emission of scattered projectile atoms following medium energy ion bombardment.   These experiments, however, suffered from low signal levels due to the low VUV photon yields. Attempts were made to build a new UHV chamber to maximize the photon collection efficiency.   Details of this chamber were given in the last technical report for this project.   It was found, however, that the VUV photon yield following medium energy ion bombardment was too low to allow reliable measurement even with

the experimental apparatus specifically designed to maximize photon collection efficiency. It was therefore decided to terminate work in this area so our resources could be more productively employed in the other areas covered by this contract.

II. Investigation of Inelastic Ion-Surface Collisions. Direct Recoil and Scattered Ion Fractions of Ne^+ on CuLi

Atoms on a surface which are directly recoiled (DR) into a forward scattering angle as a result of a direct collision from an energetic primary ion have a well defined origin and energy distribution which can be described by the binary elastic collision model (11). This is in contrast to the broad energy distributions of secondary particles which result from multiple collisions. DR events, therefore, provide an excellent means for investigating atom-surface electronic transitions and the final charge state of the direct recoiled atoms. Such studies are important to the understanding of inelastic processes in ion surface collisions. A model has recently been developed (11) for describing electronic transitions occurring during scattering of keV ions from surfaces. This model has also been extended to describing DR particles (12). The model divides the ion trajectory near the surface into three segments: (i) the incoming trajectory, (ii) the close encounter, and (iii) the outgoing trajectory. In segments (i) and (iii), electron promotion, neutralization and ionization can occur by Auger and

3

resonant charge exchange with the surface as in the treatment of Hagstrum (13). In segment (ii), the ionization and neutralization probabilities are governed by the distance of closest approach according to the Fano-Lichten mechanism (14,15). Therefore by measuring the energy dependence of the scattered and recoiled ion fractions, insight may be gained into the mechanism of charge exchange, neutralization and ionization of scattered and sputtered particles during ion-surface collisions.

A $Cu_{.12}Li_{.88}$ alloy was chosen to test this model for two reasons. First, heating the sample is known to induce thermal diffusion of the Li to the surface. Therefore by controlling the annealing time and temperature of the alloy, a surface varying in Li concentration from 12-100% can be prepared from a single sample, allowing studies of the Li coverage dependence of the scattered and recoiled particles. Also, CuLi alloys have been suggested for use as first wall and limiter materials in fusion devices (16). These alloys are of potential value in such devices because of the segregation of Li at the surface at elevated temperatures. This segregation forms a protective Li coating on the surface, preventing sputtering of Cu. The Li is sputtered primarily as a positive ion which can be reimplanted in the surface in a suitable magnetic or electric field, yielding a self sustaining surface. More information on the inelastic ion-surface processes occurring for this material is needed if it is to be used in fusion devices.

The experiments were performed on a DR-ion scattering TOF spectrometer which has been described previously (11,13). The

instrument allows the measurement of both scattered and recoiled ions and neutrals or neutrals only, allowing the determination of accurate ion fractions.

The general trends in the Ne and Li ion fractions are as follows. The Ne and Li ion fractions both increase with increasing kinetic energy of the primary ion. The Ne ion fractions increase with increasing Li coverage, while Li ion fractions decrease with increasing Li coverage. More data needs to be obtained before a detailed application of the Hagstrum/Fano-Lichten model can be made, however some qualitative conclusions can be reached.

The decrease in Li ion fraction with increasing Li coverage may be explained by the fact that an electropositive atom on the surface decreases the work function of the alloy, thus increasing the probability of Auger neutralization of the DR Li in the outgoing trajectory. Therefore, as the Li coverage increases, Auger neutralization of the recoiled Li increases, lowering the ion fraction. The increase in the Cu ion fraction with increasing Li coverage may be explained by considering electron promotions during the close encounter. Barat and Lichten (14,15) have predicted that electron excitation cross sections should rise to a maximum for collision partners with similar atomic number and then decrease with increasing atomic number. This is due to the degree of inner shell penetration of the colliding pair. Ne has a much different atomic number than both Li and Cu. However the results indicate that there is more efficient inner shell mixing in a Ne/Li collision than in a Ne/Cu collision.

5

This inner shell mixing results in electron promotion to excited and autoionizing states yielding high ion fractions. Therefore, the Ne ion fraction increases with increasing Li coverage.

This work has been completed and a manuscript is being prepared. It will be forwarded to you as soon as it is completed.

III. Investigation of Ion Induced Surface Damage of Multicomponent Targets

Work in this area has proceeded to an advanced stage. In a recently published paper (16), we reported XPS and UPS studies of 4-keV Ar^+ bombarded K_2TiF_6, K_2NbF_7 and K_2TaF_7. These studies revealed the reduction of the central metal atom to lower oxidation states upon bombardment for all of the compounds studied. The Ta and Nb in K_2TaF_7 and K_2NbF_7 were reduced to oxidation states of IV, II and 0 while the Ti in K_2TiF_6 is reduced to oxidation states of III and II. These results can be explained in terms of the thermal spike model of Kelly (17). The thermal spike model predicts that upon ion bombardment a small region near the point of impact is raised to a temperature in excess of 3000 K and that this high temperature condition exists for -10^{-11} seconds, which is several orders of magnitude longer than the vibrational period of the molecules in the surface. In this thermal spike, the molecules on the surface are atomized and ionized. Translational energy acquired by the constituents through collision cascades results in ejection of some particles

6

and random collisions with others. As the thermal spike relaxes, recombination reactions occur. The resulting decomposition products remaining on the surface are non-volatile species with high negative free energies of formation. Volatile products are lost to vacuum and products with low free energies of formation are not formed.

This model provides a good interpretation of the decomposition of the fluoroanions. Compounds of the first row transition metals with oxidation states of (II) and (III) are well known and are stable in the solid state. However, lower oxidation states in 2nd and 3rd row transition metals tend to be unstable and do not play a major role in their chemistry. As the thermal spike relaxes, stable nonvolatile products with large *free energies of formation are formed and remain on the surface.* Thermodynamics governs the probability that a species will be formed upon relaxation. Thermodynamically favorable reaction channels resulting in transition metal compounds with oxidation states of (II) and (III) are more likely for 1st row transition metals such as Ti than for 2nd and 3rd row metals such as Nb or Ta. Therefore K_2TiF_6 should have thermodynamically favorable decomposition channels which do not result in the reduction of the Ti all the way to the metal. K_2NbF_7 and K_2TaF_7, on the contrary, are less likely to have favorable decomposition channels resulting in oxidation states (II) or (III), therefore reduction to the metal is favored. A more complete description of this study is given in the attached reprint.

The thermal spike model also has been shown to provide a good description of the decomposition of transition metal oxides and oxyanions (18). These studies have shown that the thermal spike model is useful in predicting the final chemical state of species in ion bombarded surfaces. A more complete understanding of the result of ion bombardment will require an understanding of the morphology of the damaged surface. These types of studies are beyond our instrumental capabilities. Therefore no further studies are planned in this area.

IV. Dissociative Scattering of Diatomic Ions from Surfaces

A complete understanding of the dynamics of ion surface collisions requires a knowledge of the behavior of the scattering of diatomic ions from surfaces. To this end, the scattering of 1.5-4.5 keV N_2^+ from gold and graphite surfaces was studied. The scattering of molecular nitrogen ions from gold and graphite resulted in a small fraction of scattered surviving molecular ions in addition to atoms and atomic ions resulting from dissociation. This type of behavior had been observed previously (19-25). In this work the kinetic energy distributions of the scattered N_2^+ and N^+ ions were measured directly by means of an electrostatic analyzer.

The main focus of this study was to get an understanding of the mechanism of the dissociation of the molecular ions. Previous theoretical work (26-28) had treated the dissociation mechanism as a collisionally induced process arising from

8

collisional excitation of the vibrational and rotational levels of the scattered ions above the dissociation limit. This model, however, neglected the role of electronic excitation in the dissociation mechanism. Heiland and coworkers (19,20,23,25) have shown, however, that resonant electron transfer from the surface to the impinging ion is important in the dissociation mechanism of molecular ions to neutral atoms. This mechanism did not account for the small fraction of atomic ions scattered following dissociation.

Insight into the dissociation mechanism can be gained from the kinetic energy distributions of the scattered atoms and atomic ions. As stated previously, in this work these kinetic energy distributions were measured directly with an ESA. The energy spread of the dissociated atomic ions was found to be excess of 150 eV, which is much larger than can be explained by inelastic loss to the surface. This broadening, then is due to energy released in the center of mass system upon dissociation of the molecular ion. The laboratory kinetic energy spectra were transformed to relative kinetic energy distributions in the center of mass system. The relative E_k distributions of the scattered atomic ions indicate that dissociation from excited repulsive electronic states which are populated during the collision dominate the mechanism, rather than purely vibrational or rotational excitation from the $X^2\Sigma_g^+$ ground state of N_2^+. The excited dissociative $C^2\Sigma^+_u$ and $D^2\Pi_u$ states of N_2^+ are accessible by Frank-Condon transitions from the $X^2\Sigma_g^+$ state. The data are consistent with a mechanism in which these two dissociative

9

states contribute their repulsive energy to the large relative E_k distributions of the scattered N^+ ions. The electronic excitation occurs via electron promotion during the scattering collision through the Fano-Lichten mechanism.

This work is described in more detail in the attached preprint.

V. Conclusions

Significant progress has been made in the areas of research currently under investigation. The charge exchange processes of scattered and recoiled atoms are governed by inner shell penetration in the close encounter. Ion damage to multicomponent targets can be predicted by the thermal spike model. The dissociation mechanism of scattered molecular ions primarily involves electron promotion to dissociative electronic states during the collision process.

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